

CLAIMS

1. A method for the radiation grafting of a compound
that can be grafted onto a fluoropolymer, so as to
5 prevent destabilization of the fluoropolymer,
comprising the following steps:

- a) the fluoropolymer is melt-blended with a
graftable compound;
- b) the blend obtained at a) is formed into films,
10 sheets, granules or powder;
- c) the products from step b) are subjected to
photon (γ) or electron (β) irradiation with a dose of
between 0.5 and 15 Mrad; and
- d) optionally, the products from step c) are
15 subjected to a washing and/or a degassing operation,
and in which a stabilizer is blended into the
fluoropolymer.

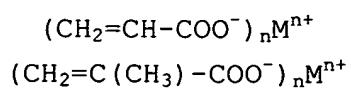
2. The method as claimed in claim 1, in which the
20 stabilizer is blended into the fluoropolymer before the
irradiation.

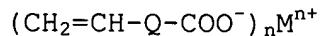
3. The method as claimed in claim 2, in which the
stabilizer is an antioxidant, a graftable metal salt or
25 else a combination of the two.

4. The method as claimed in claim 1, in which the
stabilizer is an antioxidant blended into the
fluoropolymer after the irradiation.
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5. The method as claimed in claim 4, in which a
graftable metal salt is blended into the fluoropolymer
before the irradiation.

35 6. The method as claimed in one of claims 1 to 5, in
which the stabilizer is a graftable metal salt
represented by one of the following formulae:



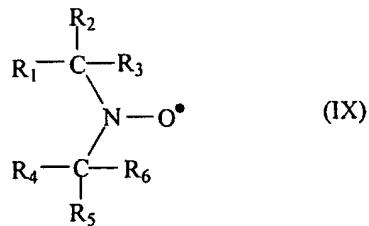


where Q denotes an optionally substituted, linear or cyclic, aliphatic or optionally substituted aromatic group and M denotes a metal cation of valence n, which
5 may be chosen from Ca^{2+} , Na^+ and Zn^{2+} .

7. The method as claimed in claim 6, in which the graftable metal salt is zinc undecylenate.

10 8. The method as claimed in either of claims 4 and 5, in which the content of graftable metal salt after step
a) is 0.1 to 10%, preferably 0.1 to 5%, of graftable metal salt per 99.9 to 90%, preferably 99.9 to 95%, of fluoropolymer.

15 9. The method as claimed in claims 3 to 8, in which the antioxidant is an alkylated monophenol, an alkylated hydroquinone, an alkylidene bisphenol, a benzyl compound, an acylaminophenol, a phosphite, a
20 phosphonite or a nitroxide of general formula:

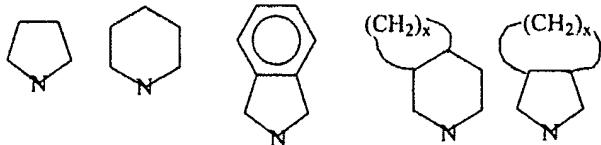


in which R_1 , R_2 , R_3 , R_4 , R_5 and R_6 denote:

25 - $C_{1-C_{20}}$, preferably $C_{1-C_{10}}$, linear or branched alkyl groups, such as methyl, ethyl, propyl, butyl, isopropyl, isobutyl, *tert*-butyl, neopentyl, whether substituted or not;

30 - $C_{6-C_{30}}$ aryl groups, whether substituted or not, such as benzyl or $C_{1-C_{30}}$ saturated cyclic aryl(phenyl) groups,

and in which the R_1 and R_4 groups may form part of an $R_1-\text{CNC}-R_4$ cyclic structure optionally substituted, possibly chosen from:



in which x denotes an integer between 1 and 12.

10. The method as claimed in claim 9, in which the
5 antioxidant is 2,6-di-*tert*-butyl-4-methylphenol, 2,6-
di-*tert*-butylphenol (IRGANOX® 140), 2-*tert*-butyl-4,6-
dimethylphenol, 2,6-di-*tert*-butyl-4-ethylphenol, 2,6-
di-*tert*-butyl-4-n-butylphenol, 2,6-di-*tert*-butyl-4-
isobutylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-
10 (β -methylcyclohexyl)-4,6-dimethylphenol, 2,6-di-
octadecyl-4-methylphenol, 2,4,6-tri-cyclohexylphenol,
2,6-di-*tert*-butyl-4-methoxymethylphenol, o-*tert*-
butylphenol, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-
6-(1'-methylundecyl)phenol, 2,4-dimethyl-6-(1'-
15 methylheptadecyl)phenol, tetrakis(3-(3,5-di-*tert*-butyl-
4-hydroxyphenyl)propionyloxymethyl)methane (IRGANOX®
1010), thiodiethylene bis(3,5-di-*tert*-butyl-4-
hydroxyhydrocinnamate) (IRGANOX® 1035), octadecyl-3,5-
di-*tert*-butyl-4-hydroxyhydrocinnamate (IRGANOX® 1076).

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11. The method as claimed in one of claims 3 to 10, in
which the antioxidant content is 0.001 to 2%,
preferably 0.001 to 1%, per 99.999 to 98%, preferably
99.999 to 99%, of fluoropolymer.

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12. The method as claimed in any one of the preceding
claims, in which the fluoropolymer is PVDF.

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13. The method as claimed in claim 12, in which the
PVDF contains at least 85% VDF by weight.

14. A structure comprising at least one layer of the
fluoropolymer modified by radiation grafting prepared
as claimed in the method of any one of the preceding
35 claims and at least one layer of another material.

15. Bottles, tanks, containers, pipes, hoses, receptacles, films and packaging produced with a structure of claim 14.

5 16. A structure comprising an inner layer in contact with the fluid to be transported or stored, consisting of the fluoropolymer modified by radiation grafting produced as claimed in any one of claims 1 to 13 and, directly attached thereto, a polyolefin outer layer.

10 17. The structure as claimed in claim 16, in which a PVDF layer is placed beside the layer of fluoropolymer modified by radiation grafting.

15 18. The structure as claimed in claim 16 or 17, in which a functionalized polyolefin layer is placed between the layer of fluoropolymer modified by radiation grafting and the polyolefin layer, said functionalized polyolefin having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer.

20 19. A structure comprising a layer consisting of the fluoropolymer modified by radiation grafting produced as claimed in any one of claims 1 to 13 and placed between two polyolefin layers.

25 20. The structure as claimed in claim 19, in which a functionalized polyolefin layer is placed between the layer of fluoropolymer modified by radiation grafting and one or both of the polyolefin layers, said functionalized polyolefin having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer.

30 35 21. A structure comprising an inner layer in contact with the fluid to be transported or stored, consisting of the fluoropolymer modified by radiation grafting produced as claimed in any one of claims 1 to 13 and,

directly attached thereto, a polyamide outer layer.

22. The structure as claimed in claim 21, in which a PVDF layer is placed beside the layer of fluoropolymer
5 modified by radiation grafting.

23. The structure as claimed in claim 21 or 22, in which a functionalized polymer layer is placed between the layer of fluoropolymer modified by radiation
10 grafting and the polyamide layer, said functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer, this functionalized polymer being compatible with the polyamide.
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24. The structure as claimed in any one of claims 16 to 23, in which the inner layer in contact with the fluid to be transported or stored may contain carbon black, carbon nanotubes or any other additive capable
20 of making the structure conducting in order to prevent the build-up of static electricity.

25. A structure comprising an outer layer consisting of the fluoropolymer modified by radiation grafting
25 produced as claimed in any one of claims 1 to 13 and, directly attached thereto, a layer of a substrate.

26. The structure as claimed in claim 25, in which a PVDF layer is placed beside the layer of fluoropolymer
30 modified by radiation grafting.

27. The structure as claimed in claim 25 or 26, in which a functionalized polymer layer is placed between the layer of fluoropolymer modified by radiation
35 grafting and the substrate layer, said functionalized polymer having functional groups capable of reacting with the functional groups grafted onto the fluoropolymer, this functionalized fluoropolymer being compatible with the substrate.

28. A fluoropolymer onto which a graftable compound is radiation-grafted, said fluoropolymer being stabilized by one or more antioxidants.

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29. A fluoropolymer onto which a graftable compound is radiation-grafted, said fluoropolymer being stabilized by a graftable metal salt and by one or more antioxidants.

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30. The fluoropolymer as claimed in claim 28 or 29, in which the antioxidant content is 0.001 to 2%, preferably 0.001 to 1%, per 99.999 to 98%, preferably 99.999 to 99%, of fluoropolymer.

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31. A fluoropolymer onto which a graftable compound is radiation-grafted, said fluoropolymer being stabilized by a graftable metal salt.

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32. The fluoropolymer as claimed in one of claims 29 to 31, in which the content of graftable compound grafted, that is to say linked to the fluoropolymer via a covalent bond, is 0.1 to 5%, preferably 0.1 to 2.5%, per 99.9 to 95.0%, preferably 99.9 to 97.5%, of fluoropolymer.

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33. The fluoropolymer as claimed in one of claims 29 to 32, in which the content of grafted metal salt, that is to say that links to the fluoropolymer via a covalent bond, is 0.1 to 5%, preferably 0.1 to 2.5%, per 99.9 to 95.0%, preferably 99.9 to 97.5%, of fluoropolymer.

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34. The fluoropolymer as claimed in one of claims 29 to 33, in which the graftable metal salt is zinc undecylenate.

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35. The fluoropolymer as claimed in one of claims 29 to 33, in which the graftable metal salt is calcium

undecylenate.

36. The fluoropolymer as claimed in one of claims 29
to 33, in which the graftable metal salt is sodium
5 undecylenate.

37. The fluoropolymer as claimed in one of claims 28
to 36, in which the fluoropolymer is PVDF.

10 38. The fluoropolymer as claimed in claim 37, in which
the PVDF contains at least 85% PDF by weight.